

28 pages
IN-18346REVIEW OF METHODS FOR PREPARATION OF ZINC
AND CADMIUM SULFIDE, SELENIDE AND TELLURIDE SINGLE CRYSTALS

Mieczyslaw Kucharczyk, Krystyna Zabłudowska

Translation of "Przegląd metod otrzymywania monokryształów siarczków selenków i tellurków cynku i kadmu", Zeszyty Naukowe Politechniki Białostockiej. (Ser) Matematyka Fizyka, Chemia, Poland, 1976, No. 1, pp. 3-21.

(NASA-TM-88426) REVIEW OF METHODS FOR
PREPARATION OF ZINC AND CADMIUM SULFIDE,
SELENIDE AND TELLURIDE SINGLE CRYSTALS
(National Aeronautics and Space
Administration) 28 p

N86-29692

Unclass

G3/76 43454

REVIEW OF METHODS FOR PREPARATION
OF ZINC AND CADMIUM SULFIDE, SELENIDE AND TELLURIDE
SINGLE CRYSTALS

Mieczyslaw Kucharczyk, Krystyna Zabłudowska

1. INTRODUCTION

In recent years, in the field of studies of the luminescence of crystalline phosphors, one can observe an increasing number of works dealing with monocrystals while studies whose objects are polycrystalline powders are on the decrease. We shall not be far from the truth when we maintain that one of the main reasons for this situation is the difficulty encountered when attempting to interpret theoretically the results of experimental studies concerning polycrystalline powders. For, we cannot neglect the effect of grain boundaries of polycrystalline powder on its optical and electrical properties. And consideration of this effect when comparing experimental results with those expected from the theory of solid state, which strictly speaking concerns monocrystals, is not feasible in the majority of cases.

Current studies of photoluminescence and electroluminescence at the Department of Physics of the Bialystok Polytechnic Institute are based on the compounds $(\text{Zn}, \text{Cd})\text{S}$ and $(\text{Zn}, \text{Cd})\text{Se}$ activated with various admixtures exclusively in the form of polycrystalline powders. The intended commencement of studies of the monocrystals of these compounds requires the selection and mastering of a method for growth of monocrystals of $(\text{Zn}, \text{Cd})\text{S}$ and $(\text{Zn}, \text{Cd})\text{Se}$, which would correspond to the conditions and possibilities of the Department.

The aim of this paper is to review the existing methods for preparation of monocrystals of the compounds (Zn, Cd)S, (Zn, Cd)Se and also (Zn, Cd)Te, and to recommend a method which, under conditions of the Physics Department of the Bialostok Polytechnic Institute, would be the most suitable for realization.

2. CLASSIFICATION OF PROCESSES FOR GROWTH OF MONOCRYSTALS

There is at present a multitude of methods for obtaining monocrystals and it is desirable, therefore, to classify them suitably. A very useful classification can be obtained if we take for the criterion the analysis of the state of thermodynamic equilibrium, the deviation from which leads to the growth of monocrystals /1/.

The process of the growth of monocrystals is a heterogeneous chemical reaction of the type:

- a) solid \rightarrow crystal
- b) liquid \rightarrow crystal, or
- c) gas \rightarrow crystal

If such reaction takes place in a system in which there is only one component, namely the material undergoing crystallization, and the traces of impurities or concentration of intentionally added admixtures are very small, then the growth of crystal under such conditions is called the one-component crystallization.

Laudise /1/ classifies processes of one-component crystallization according to the following scheme:

A. Solid \rightarrow Solid

- annealing in the presence of applied stresses (removal of stresses),
- recrystallization,
- polymorphous transitions,
- sintering.

B. Liquid ---> Solid

- Conservative processes (in which the total amount of material in two phases, liquid and solid, remains the same, i.e. the material is not supplied from outside and is not expelled from one or the other phase, that is, only solidification occurs):
 - a) directional solidification (the Bridgeman-Stockbarger method),
 - b) cooling of nucleus (the Kyropoulos method),
 - c) drawing (the Czochralski method)
- Nonconservative processes (the material may be introduced into the molten zone by means of any chosen process except the crystallization):
 - a) zone melting (horizontal, vertical, the method of fluid zone, growth on the base),
 - b) the Verneuil method (flame, plasma melting).

C. Gas (vapor phase) ---> Solid

- sublimation - condensation
- evaporation.

If in the composition, in addition to material which undergoes crystallization, there is present a large concentration of admixture (additive), such that the crystallizing material is actually dissolved in solvent or arises as a result of chemical reaction, then this case is called the multicomponent crystallization. Laudise /1/ divided the multicomponent growth processes as follows:

A. Solid --> Solid

- precipitation from solid solution.

B. Liquid --> Solid

- Growth from solution (evaporation, slow cooling at temperature differences and zone dissolving at temperature gradient):

- a) water solvents,
 - b) organic solvents,
 - c) liquid salt solvents,
 - d) solvents under subcritical conditions
(e.g., hydrothermal conditions),
 - e) other inorganic solvents (metals).
- Growth as a result of occurring reaction (in the same media as above, but with change of temperature or concentration):
- a) chemical reactions,
 - b) electrochemical reactions.
- C. Gas (Vapor phase) \rightarrow Solid
- Growth as a result of reversible reactions (change of temperature or concentration):
- van Arkel method (deposition on glowing thread).
- Growth as a result of irreversible reactions:
- epitaxial growth.
- D. Combined (Vapor \rightarrow liquid \rightarrow solid).

We shall consider now the application of these particular methods for preparation of monocrystals of the compounds (Zn, Cd)S, (Zn, Cd)Se and (Zn, Cd)Te.

3. THE "SOLID-SOLID" GROWTH METHOD

This method consists of heating the polycrystalline substance, in the process of which there occurs an increase of initially small grains. The method is applied primarily, although not exclusively, for preparation of monocrystals of metals.

Among the main advantages of this method we should mention the possibility of carrying the growth process at low temperatures without additional components, and possibility of obtaining

a monocrystal of desired shape, which is of great importance in monocrystallization of metals. In monocrystals obtained by this method the distribution of additives is the same as in the initial material. On the other hand, the disadvantages of this method are a high density of crystallization centers, a very limited possibility of controlling the formation of nuclei, and consequently difficulties in obtaining large monocrystals.

Monocrystals of metals are obtained in the process of annealing in the presence of applied stresses, and of nonmetallic substances - in the process of sintering. According to theoretical analysis of the kinetics of sintering done by Laudise /1/, the sources of the motive force of this process are as follows:

- residual deformations,
- effects of grain orientation,
- effect of the size of grains.

Mikulyak /3/ obtained monocrystals of CdS and CdS:Te with sizes of the order of centimeter by a method close to the process of sintering. Polycrystalline charge was placed in a quartz ampoule of diameter about 1.2 cm and length 5-15 cm in which, before sealing, the air was pumped off to 10^{-5} - 10^{-6} Tr. The ampoule was placed in a multizone furnace at a temperature between 930°C and 1030°C in the part of furnace with lower temperature gradient so that the end of ampoule with charge was located at a lower temperature. The diagram of this furnace together with a typical temperature profile are presented in Figure 1.

After 12 to 64 hours, depending on the amount of material and the temperature of heating, the polycrystalline material was joined together into the monocrystalline sample. Mikulyak /3/ calls this process coalescence. Tests showed that the distribution of additive (Te) in the monocrystalline sample was the same as in the polycrystalline initial material. The process of coalescence studied by Mikulyak reminds of the "Ostwald ripening" in solutions,

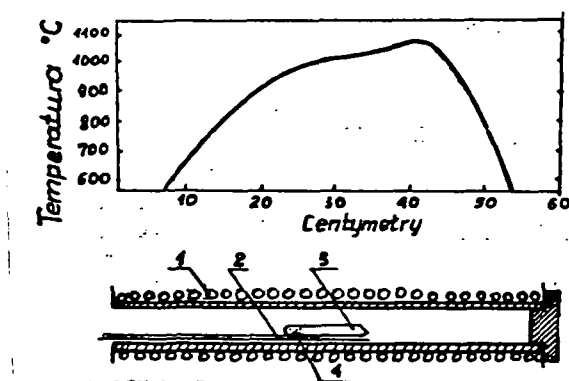


Figure 1. Temperature profile and cross-section of furnace used by Mikulyak /3/ for coalescence of CdS:
1 - Kanthal wire, 2 - thermocouple,
3 - ampoule, 4 - charge.

where large crystals grow at the cost of smaller ones, but here this process proceeded faster than in solutions. The mechanism of coalescence is not yet accurately known, and further studies are necessary to clarify whether it is not based on an intermediate role of vapor phase. One can only assume, what appears to be very probable, that the motive force of the process of coalescence is connected with effects of the size of grains.

4. GROWTH OF MONOCRYSTALS FROM LIQUID PHASE

In the one-component system the growth of monocrystals according to scheme liquid \rightarrow solid leads to obtaining monocrystals from a molten substance. In comparison with other processes, the process of obtaining single crystals from a molten substance may be controlled and is relatively best studied. It is not, however, universal since it is not possible to obtain monocrystals of many substances by this method because of the following reasons:

- a) the material undergoes decomposition even before melting, or melts incongruently,
- b) the substance undergoes strong sublimation or has too high vapor pressure at the melting temperature,
- c) the desired polymorphous structure is unstable at the contact with molten material,
- d) the melting temperature is so high that the growth of monocrystals from a molten substance is practically impossible,
- e) it is impossible to introduce the required activator at the given conditions of growth.

Uncontrolled solidification of a molten substance leads to obtaining the final product in the form of polycrystalline mass. Hence the basic goal of each method of crystallization from molten substance is to attain the controlled formation of crystallization nuclei in such a way that the subsequent growth proceeds on one or only few nuclei. For this purpose we utilize the controlled temperature profile, enabling to localize the area of the highest supercooling of liquid in a small section in the vicinity of the nucleus. A simple to realize and ingenuous method to control the supercooling, necessary for production of monocrystals, has been developed in the method of Bridgman-Stockbarger, described in the works /1/ and /4/. Now we shall try to learn more about this method.

In the Bridgman-Stockbarger method the molten material undergoing crystallization is placed in a cylindrical crucible, which is lowered in the field of temperature gradient (Figure 2), or the furnace is raised along the crucible. As a result, the boundary of separation of monocrystal and molten mass is always at the constant temperature (supercooling).

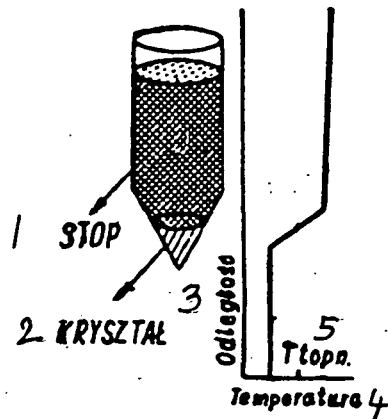


Figure 2. Temperature distribution in the Bridgman-Stockbarger method with movable crucible - according to work /1/.

1 - melt, 2 - crystal, 3 - distance
4 - temperature, 5 - melting temperature.

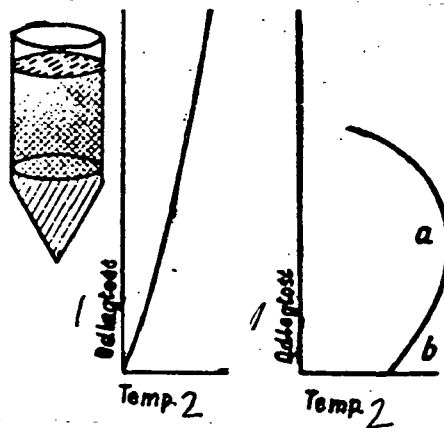


Figure 3. Temperature distribution in the Bridgman-Stockbarger method with stationary crucible - according to work /1/.

1 - distance, 2 - temperature.

A similar effect can be achieved in the case of a stationary crucible in a cooling down furnace with an initial constant temperature gradient (Figure 3).

The crucible should have such a shape that solidification of molten mass begins at one point (in the narrow part of the

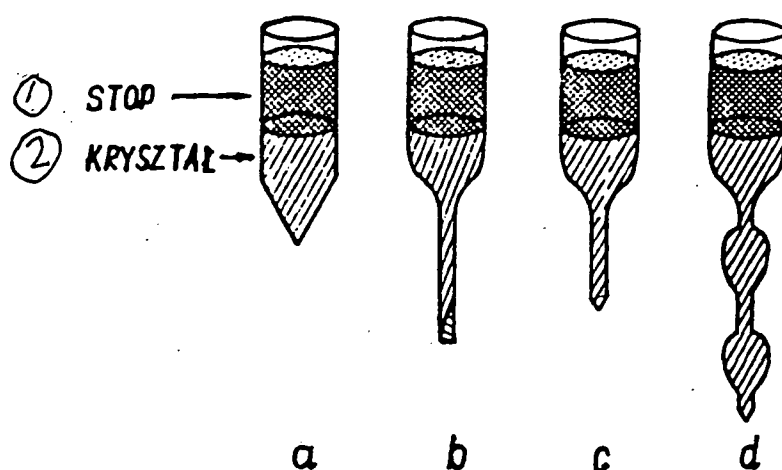


Figure 4. Shapes of crucibles used to obtain monocrystals by the method of Bridgman-Stockbarger - according to work /1/.
1 - molten material, 2 - crystal

crucible) and only a small number of crystallization nuclei are formed. The shape of the crucible should also ensure a certain advantage to one of the crystals at the boundary between the monocrystal and molten substance. Figure 4 shows several crucibles with shapes suitable for this purpose:

- a) A cylindrical crucible with cone-shaped bottom ("natural" selection) - Figure 4a. This form of the bottom ensures that in the initial phase only a small volume of molten material becomes supercooled and only one crystallization nucleus is formed. If several nuclei should form, then in the whole separation boundary one particular nucleus, with orientation most suitable for growth, will soon become dominant.
- b) A cylindrical crucible with capillary end - Figure 4b. Initially the molten material undergoes supercooling also in very small volume. Because of the capillary there is great likelihood that, in the case of formation

of several crystallization nuclei, during the movement of crystallization front one of the small crystals will grow to such an extent that it will occupy the whole area of interface.

- c) The end of the capillary tube has the cone shape - Figure 4c. This arrangement combines the effects characteristic of the first and the second type of crucible.
- d) The end of a cylindrical crucible with cone bottom has one or two broadenings connected with narrow parts (selection by narrowing) - Figure 4d.

In the Bridgman-Stockbarger method the shape of the crucible, the temperature gradient and the velocity of moving the crucible (or the rate of cooling down the furnace) are selected empirically. The material from which the crucible is made should be suitable for the substance undergoing monocrystallization, for atmosphere and the temperature of growth. And the furnace should be constructed in such a way that it ensures the desired gradient of temperature.

Direct application of the above described Bridgman-Stockbarger method for preparation of the monocrystals of compounds (Zn, Cd)S, (Zn, Cd)Se and (Zn, Cd)Te encounters a number of difficulties of a technical nature. The reasons for these problems are the high melting temperature of these substances (e.g., the melting temperature of ZnS is about 1850°C) and a considerable (of the order of several tens of atmospheres) vapor pressure of these compounds. Only CdTe (melting temperature 1092°C) can be obtained by the conventional Bridgman-Stockbarger method.

According to work /5/, preparation of monocrystals of remaining compounds discussed hereby by the Bridgman-Stockbarger method requires the use of high-pressure containers. The high-pressure version of the Bridgman-Stockbarger method allows to prepare large monocrystals of ZnS, ZnSe, CdS, CdSe and also

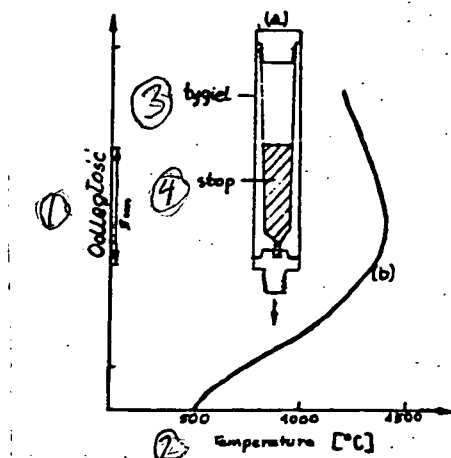


Figure 5. Cross-section of praphite crucible and typical temperature distribution in a high-pressure furnace - according to work /7/.

- 1 - Distance, 2 - Temperature
- 3 - crucible, 4 - molten material

mixed monocrystals, e.g., $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ and $\text{ZnS}_x\text{Se}_{1-x}$. Kozielski /6/ describes the apparatus and procedure used to obtain mixed monocrystals.

H. Kimura and H. Komiya /7/ studied deviations from stoichiometry of the composition of monocrystals ZnS , CdS , ZnSe , ZnTe and CdSe prepared in a high pressure Bridgman furnace. The high-pressure furnace used by them had a graphite heating element, and in the process of crystal growth it was filled with argon under the pressure of about 100 atm. The graphite crucible containing the molten mass was moved by a mechanism which was outside the furnace, with which it was coupled magnetically. The cross-section of the crucible and the temperature profile are shown in Figure 5. The composition of monocrystals studied by these researchers was stoichiometric for ZnS , with excess of Cd for CdS and with excess of Se and Te for selenides and tellurides.

In another version of the Bridgman-Stockbarger method the furnace is set horizontally, and the molten substance is

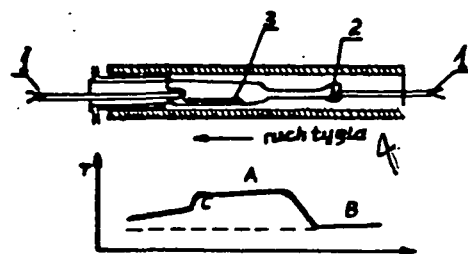


Figure 6. Horizontal method for obtaining CdTe:

- 1 - thermocouple, 2 - Cd,
- 3 - pointed quartz boat with CdTe, 4 - movement of crucible - according to work of Kroger and De Nobel/8/.

contained in a refractory boat which is moved in a horizontal temperature gradient /4/. In this way Kroger and de Nobel /8/ obtained CdTe crystals. A quartz boat with pointed end was covered on surface with carbon and filled with cadmium telluride. This vessel with cadmium telluride was placed at one end of the quartz tube, and metallic cadmium was placed at the other end. The scheme of the used furnace and the temperature gradient are presented in Figure 6. The possibly highest gradient was chosen and the temperature was accurately regulated in the areas A and B. The monocrystal nucleus was placed in the sharp pointed end of the boat, and to the right of the nucleus there was the molten mass. The velocity of moving the crucible was 1 cm/hour. The pressure of cadmium vapor in the area B, and consequently the contents of cadmium in the obtained monocrystal, was regulated by the temperature. As is seen, an advantage of the horizontal version of the Bridgman-Stockbarger is possibility of the regulation of stoichiometric composition of the obtained monocrystal.

ORIGINAL PAGE IS
OF POOR QUALITY

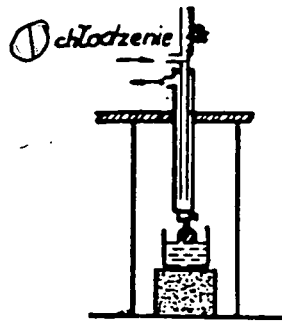


Figure 7. Principle of the drawing of monocrystals -
according to work /4/.
1 - cooling

An earlier technique than the method of Bridgman-Stockbarger is the method of Czochralski for the drawing of monocrystals from a molten substance, described in works /1/, /4/. In this method a small monocrystalline nucleus is made to contact the surface of molten substance and then is withdrawn slowly. The temperature has to be regulated so that it is somewhat lower than the temperature of molten substance, for only then there is solidification of the substance and growth of the nucleus. The velocity of drawing must correspond to the velocity of growth of monocrystal so that the growing monocrystal remains in contact with the melt and the surface of contact stays at a constant temperature. With suitably careful drawing one can produce a large monocrystal from a small nucleus. The principle of the drawing of monocrystals is illustrated in Figure 7. The method of Czochralski has an advantage over the method of Bridgman-Stockbarger in application to substances which increase their volume on solidification, since it allows to avoid the mechanical effect of the crucible on the growing monocrystal.

There are many modifications of the method of Czochralski, but their description would be too lengthy and we shall not deal with them here.

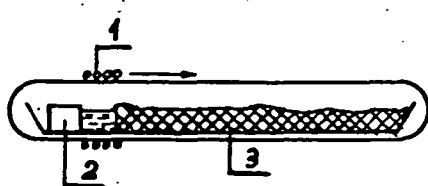


Figure 8. Arrangement for obtaining monocrystals by the method of zone melting: 1 - heater, 2 - nucleus, 3 - polycrystalline bar - according to work /4/.

A relatively new technique, in comparison with methods of Czochralski and Bridgman-Stockbarger, was introduced in 1952 by Pfann /9/. It is the zone melting method, which has become now the principal method for purification of semiconductors. The formation of monocrystals in the process of purification indicated that the method can be used successfully for preparation of monocrystals. The idea of this method is shown in Figure 8. A monocrystalline nucleus is placed at one end of the crucible which is in the shape of a boat, and the rest of the crucible is filled with polycrystalline substance. A movable heating element is used to melt partly the nucleus (to obtain pure surface of growth), and then this element moves slowly also causing the molten zone to move slowly along the polycrystalline material to the opposite end of the crucible.

As we pointed out, monocrystals of sulfides, selenides and tellurides have high vapor pressure at the melting temperature. Therefore, they can also be obtained by the method of zone melting, using the apparatus shown in Figure 9. By means of an additional stationary heater the whole bar is kept at a temperature somewhat lower than the melting temperature of the substance, reducing thereby the evaporation of the compound from the zone. A container with the volatile compound

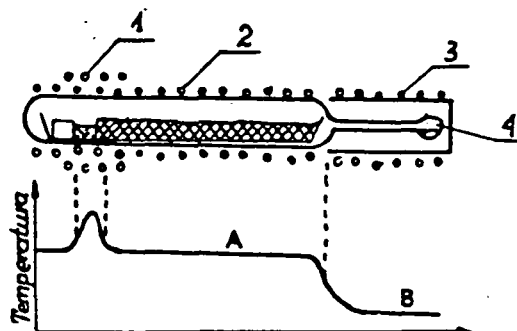


Figure 9. Scheme of apparatus for producing sulfides, selenides and tellurides: 1 - zone heater, 2 - bar heater, 3 - container heater, 4 - container for volatile component - according to work /4/.

allows to regulate the stoichiometric composition. Since the basic destination of the method of zone melting is purification of substance from admixtures, its application to the growth of monocrystals gives possibility of regulating the contents of additives in the obtained monocrystal. It is one of the most important advantages of the method.

5. PRODUCTION OF MONOCRYSTALS FROM VAPOR PHASE

The ease of transition of compounds A^2B^6 into a gaseous state with simultaneous decomposition before reaching the melting temperature allows to produce monocrystals of these compounds from vapor phase by the sublimation-condensation method. High vapor pressure of both components enables to transport them through the gas phase, which is the idea of this method.

The transport of material in the gas phase may take place either in a dynamic or static way. In the dynamic method, inert gas serves as a carrier; its steady stream flows through the

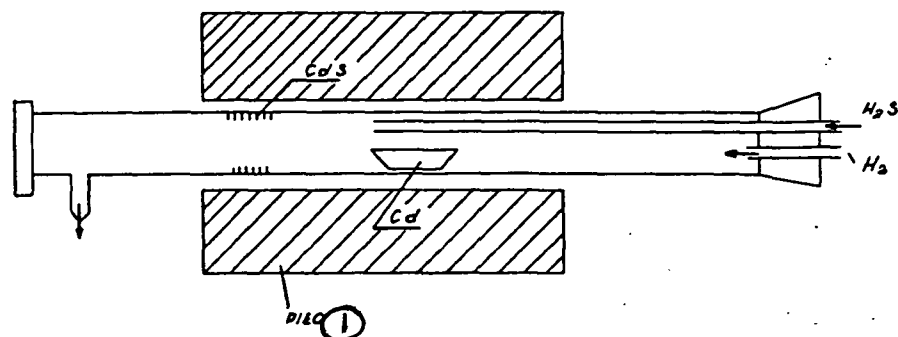


Figure 10. Furnace for producing monocrystals by the method of Frerichs - according to work /10/. 1 - furnace

system. Using this technology, Frerichs /10/ obtained the first monocrystalline samples of CdS in the form of platelets and needles. The process was carried out as follows. Cadmium was loaded into a quartz boat, which was placed inside a quartz tube, and put inside the furnace at temperature ensuring the formation of metal vapor. A slow stream of hydrogen or inert gas was directed to this metal vapor. This gas stream carried the metal vapor to the place of the inlet of tubing which supplied H₂S. Combination of both streams, of H₂S and metal vapor, initiated reaction of the synthesis of CdS (Figure 10).

In the static method of transport we utilize the diffusion in the gas phase, through which dissociation products of A^2B^6 compounds are transported to crystallization sites, that is, to cooler areas of the reaction ampoule. This method was used for the first time by Reynolds and Czyzak /11/, and was modified by Green and coworkers /12/. Further modification was introduced by Piper and Polich /13/. The scheme of the furnace, with temperature distribution, used by Piper and Polich to obtain CdS monocrystals is shown in Figure 11. The ampoule was loaded with

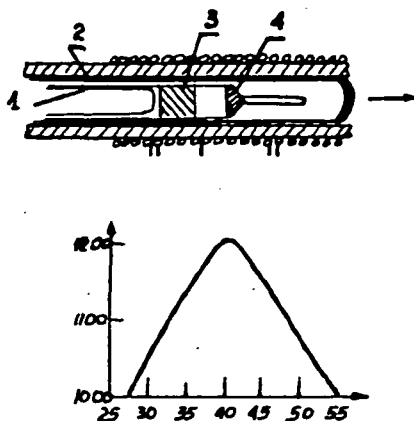


Figure 11. Cross-section and temperature distribution of furnace used to obtain CdS from vapor phase: 1 - crucible, 2 - Alundum pipe, 3 - charge, 4 - monocrystal - according to Piper and Polich /13/.

polycrystalline CdS. A crucible with cone ending was placed in an evacuated quartz ampoule which was then filled with argon under the pressure of 1 atm. The crucible made tight contact with internal walls of the ampoule. The ampoule with crucible was moved slowly in the direction shown by arrow in Figure 11 to cooler parts of furnace with velocity 0.3-1.5 mm/hour.

The optimal conditions of growth, hence the temperature gradient, velocity of moving the crucible, and composition and pressure of gases introduced to the vessel with the charge, were selected experimentally. The characteristic feature of this method is that the growth begins in the capillary part of the ampoule, so that the necessity of the application of nucleus is eliminated.

Current literature contains many works dealing with the "sublimation-condensation" method.

In Poland, the following centers among others are working on obtaining monocrystals of A^2B^6 compounds from vapor phase:

Physics Institute of the Polish Academy of Sciences, Physics Department of Warsaw University, Military Technological Academy (WAT) - studies by Zmija /2/, /14/, Copernicus University in Torun - studies of Lozykowski /17/. Using the method described by Piper and Polich, Zmija and Nowak /14/ obtained monocrystals of CdS with diameter 10-20 mm and length 25-70 mm. They found that the growth conditions, that is the suitable temperature gradient, velocity of moving the ampoule, dimensions and shape of the ampoule, and degree of purity of the ampoule and initial substance have a decisive effect on the quality and size of obtained monocrystals. According to them, a longer time of residence and decomposition of vapor in the hot crystallization zone improve the quality of monocrystals.

Bulakh and Pekar in their works /15/ and /16/ investigated the effect of the shape of ampoules on the quality of monocrystals from vapor phase in sealed ampoules.

Clark and Woods /18/ obtained monocrystals from vapor phase in the horizontal and vertical position. The process of growth in horizontal position did not differ basically from that proposed by Piper and Polich. But the growth in vertical position was taking place as follows. After the preliminary purification of the charge by double vacuum sublimation in quartz ampoules placed in a two-zone furnace, the purified CdS was placed in a quartz ampoule as shown in Figure 12. The ampoule ending with a cone having the opening angle 30° was connected with a quartz rod supporting the ampoule and conducting away the heat in the initial stage of growth of the monocrystal. After pumping off the ampoule to pressure of the order of 10^{-6} Tr, it was filled with spectrally pure argon under the pressure 200 Tr. Charges of S or Cd were placed in the lower part of the apparatus. The ampoule was placed in the furnace in such a way that the growth capillary and the charge were at the maximal temperature (1165°C),

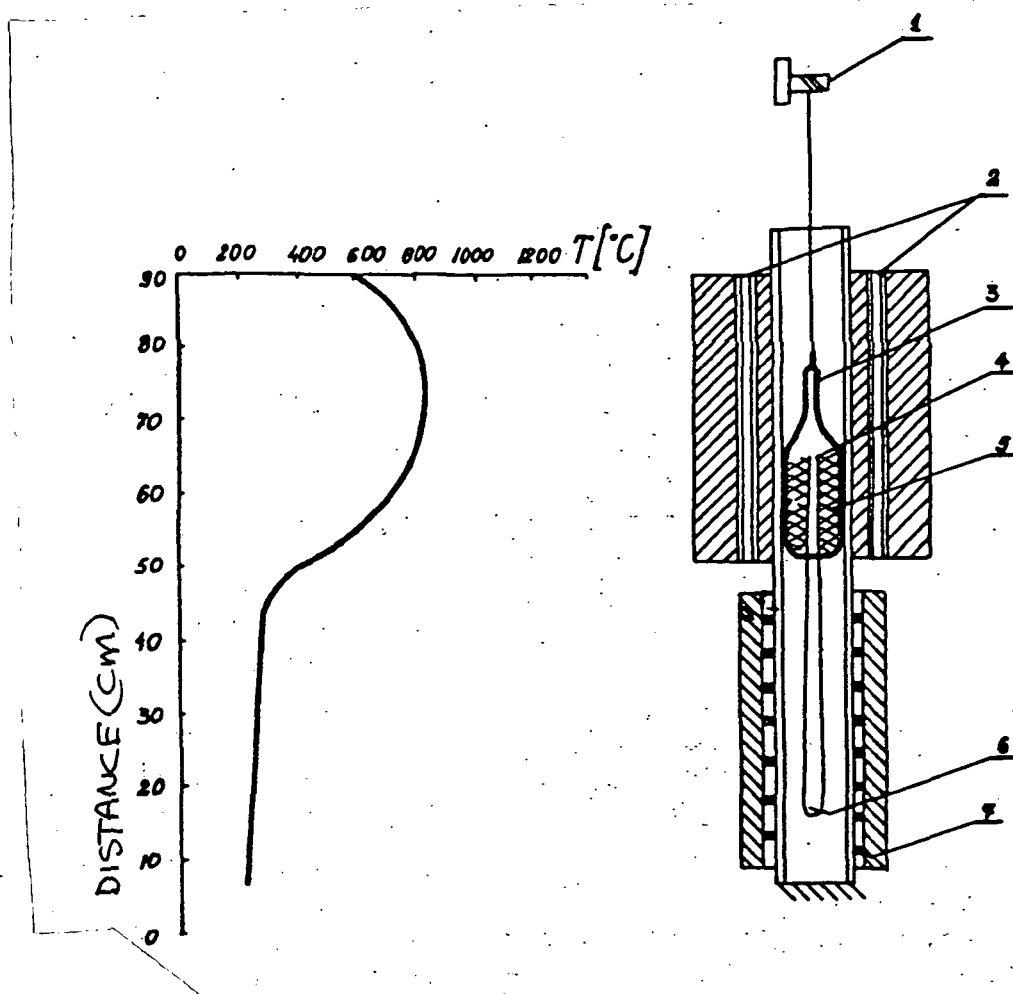


Figure 12. Two-zone furnace in the vertical method of sublimation-condensation: 1 - drive, 2 - heating (?), 3 - growth capillary, 4 - inlet for vapor of material regulating stoichiometry, 5 - polycrystalline CdS, 6 - source of sulfur or cadmium, 7 - winding - according to Clark and Wood /18/.

and the excess Cd (or S) at a lower temperature. After 20 minutes the drive was started. The growth ampoule was moving upwards with the velocity 0.6 mm/hour. The process of growth lasted about 150 hours. Next, the monocrystals were cooled in two ways:

- a) by removing the ampoule from the furnace, the fast process,
- 6 b) by leaving the ampoule in the cooling furnace, the slow process. The obtained monocrystals differed qualitatively.

Clark and Woods noticed that crystals obtained in a vertical furnace had defects in the form of empty spaces (voids). They maintain that these voids arise either in growth under conditions close to stoichiometric ones, when sublimation proceeds rather fast, or in the slow growth. In the first case, the voids are ordered, which is connected with a large temperature gradient or a fast movement. These conditions create a considerable supersaturation of vapor in the plane of growth, hence the formation of growth spirals on the voids. The application of vertical furnace allows to obtain A^2B^6 monocrystals with controlled deviations from stoichiometry by creation of suitable partial pressures of components over the growing monocrystal. These deviations from stoichiometry decide the physical and electrical properties. This matter is very important when we want to obtain monocrystals with desired specific optical and electrical properties. In the horizontal method of growth the physical and electrical properties are corrected in the course of long-lasting processes of selfdiffusion.

Preparation of CdS is the topic of the largest number of publications in the literature dealing with studies concerned with obtaining A^2B^6 compounds.

The same methods are applicable also, with a high degree of success, to preparation of ZnSe, ZnTe and CdTe.

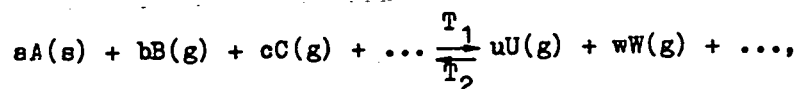
Burr and Woods /19/, and Lozykowski /17/, obtained ZnSe monocrystals using the vertical and horizontal furnace techniques. Polycrystalline ZnSe used by Burr and Woods in a vertical ampoule sublimed at the temperature 1150°C to the upper vessel where the growth was taking place at the temperature 1100°C . Zn was in excess

in this process. Metallic zinc was kept at the temperature 555°C . The velocity of moving the ampoule was 17 to 35 mm/24 hours. It was found that in this range the quality of obtained monocrystals ZnSe did not depend on the velocity of move. But the quality was highly dependent on the location of placing the excess of zinc. If the excess Zn was placed directly at the bottom of ampoule, the transport was increasing and monocrystals of ZnSe 3-4 centimeters long were obtained during 140 hours. On the other hand, if the excess Zn was placed near the charge, the transport was slower and the growth of crystals was poorer. The crystals of ZnSe obtained in the horizontal furnace were of better quality than those produced in the vertical furnace.

Applying the sublimation-condensation method, Lauer and Williams /20/ obtained mixed monocrystals (Zn, Cd)S and (Zn, Cd)Te. The mixed monocrystals of these compounds are semiconductors with a large positive energetic gap. The width of this energy gap can be regulated by changing the percent composition of the crystals.

It is also worth saying something about the newest technique for production of monocrystals from gas phase through chemical transport. The method of chemical transport was applied to A^2B^6 compounds for the first time by Nietzsche /21/. The method consists of transporting through gas phase of a solid material from an area of temperature T_1 to an area of temperature T_2 by means of a carrier substance. This substance fulfills its role only when between it and the solid material occurs a heterogeneous reversible reaction, which leads to the formation of only gaseous products of reaction according to the equation:

(1)



where:

- A(s) - solid material being transported (e.g. CdS)
- B(g), C(g) - carrier substances (e.g., J_2^2)
- U(g), W(g) - gaseous products of reaction (e.g. CdJ₂ and S₂)
- a,b,c...u,w - number of moles of A,B,C...U,W

The temperatures are chosen in such a way that at T_1 the reaction proceeds to the right, and at T_2 - to the left. The reaction described by this equation is the chemical transport reaction.

The most difficult problem in the technique of chemical transport is the choice of a suitable transporting substance (carrier), i.e. such that the transporting chemical reaction creates large differences of pressures at low differences of temperatures. Small temperature gradients necessitate the use of ampoules in vertical position since it facilitates partly the convection of gases. Small differences of temperature entail small velocity of transport. Thus to obtain a large monocrystal (of several cm³) it is necessary to spend the time of several weeks or even more than ten weeks.

The advantage of this technique, however, is that it can be applied even in cases when crystallization from the molten mass is not possible, because

- the substance decomposes before reaching the melting temperature,
- it undergoes a phase transition at high temperature.

Even when monocrystals can be obtained by one of the earlier known methods, the chemical transport sometimes proves to be the most convenient, since crystallization in chemical transport may take place at a considerably lower temperature. For instance, ZnS crystallizes from the molten mass at the temperature of about 1830°C under the pressure 12 atm. of argon; crystallization from

gas phase through sublimation in vacuum or in the atmosphere of inert gas takes place at the temperature of about 1300°C ; and crystallization from gas phase by chemical transport with iodine requires the temperature of about 750°C . Thanks to crystallization at low temperatures it is possible to obtain structurally pure, low-temperature polymorphic varieties. Here again we can take advantage of an example of ZnS /22/: by means of chemical transport with iodine we can obtain at the temperature $850\text{--}750^{\circ}\text{C}$ monocrystals with structure of sphalerite, but at the temperature $1170\text{--}1150^{\circ}\text{C}$ monocrystals with structure of wurtzite.

Methods of obtaining monocrystals from vapor phase continue to be studied and intensively developed, because they allow to produce monocrystals with relatively low density of dislocations, with regulated deviations from stoichiometry, and with programmed physical and electrical properties.

6. CONCLUSIONS

On the basis of our relatively short review of the methods for production of the monocrystals of compounds $(\text{Zn}, \text{Cd})\text{S}$, $(\text{Zn}, \text{Cd})\text{Se}$ and $(\text{Zn}, \text{Cd})\text{Te}$ we can draw the following conclusions:

1. The "solid \rightarrow solid" methods are not used actually for production of monocrystals of these compounds.
2. The methods for obtaining monocrystals from a molten substance are well developed and have many advantages. However, in application to compounds of our interest they require the use of a complicated and expensive high-pressure apparatus.
3. The most suitable method under conditions of the Department

of Physics of Bialystok Polytechnic Institute is the method of sublimation-condensation, since it does not require the use of a too complex and difficult to obtain apparatus, and yet it allows to obtain monocrystals which are satisfactory structurally, with regulated deviations from stoichiometry. Many centers in our country study and develop this method further. Cooperation with these centers will allow us to initiate faster the production of monocrystals required to perform studies in the area of luminescence.

REFERENCES

1. Laudise: Growth of monocrystals (Transl. from English to Russian)
2. Zmija: Some problems in obtaining monocrystals from a vapor phase (manuscript)
4. Lawson: Production of monocrystals
9. Pfann: Zone melting (In Russian)
17. Lozykowski: Proceedings of the Conference on Technology of Monocrystals (manuscript)

- [1] LAUDISE R., PARKER R.: Wzrost monokryształów, wyd. "Mir" Moskwa, 1974 (Tłum. z angielskiego na ros.).
- [2] ŻMIJA J.: Niektóre problemy otrzymywania monokryształów z fazy pary, "Technologia monokryształów" część 1, referaty I Ogólnopolskiego Seminarium Technologii Monokryształów, Szklarska Poręba 18 - 27 października 1972, PWN, Warszawa, 1974 (na prawach rękopisu).
- [3] MIKULYAK R.M.: J. Cryst. Growth, 8, 149 (1971).
- [4] LAWSON W.D., NIELSEN S.: Otrzymywanie monokryształów, PWN, Warszawa, 1962.
- [5] GIRIAT W.: Postępy Fizyki, 23, 329 (1972).
- [6] KOZIELSKI M.: J. Cryst. Growth, 1, 293, (1967).
- [7] KIMURA H., KOMIYA H.: J. Cryst. Growth, 20, 283 (1973).

- [8] KROGER F.A., de NOBEL D.J.: Electronics, 1, 190, (1955).
- [9] PFANN W.: Złotego pławka, wyd. "Mir", 1970.
- [10] FRERICH S.: Phys. Rev., 72, 594 (1947).
- [11] REYNOLDS D.C., CZYZAK S.J.: Phys. Rev., 79, 543 (1950).
- [12] GREEN L.C., REYNOLDS D.C., CZYZAK S.J., BAKER W.M.: J. Chem. Phys., 29, 1375 (1958).
- [13] PIPER W., POLICH S.J.: J. Appl. Phys., 32, 1278 (1961).
- [14] ŻMIJA J., NOWAK T.: Biul. WAT, 121, 208 (1969).
- [15] BULAKH B.M., PEKAR G.S.: J. Cryst. Growth, 7, 375, (1970).
- [16] BULAKH B.M., PEKAR G.S.: J. Cryst. Growth, 8, 99, (1970).
- [17] ŁOŻYKOWSKI H.: Materiały I Ogólnopolskiego Seminarium Technologii Monokryształów, Szklarska Poręba 18 - 27 października 1972, PWN, Warszawa, 1974 (na prawach rękopisu).
- [18] CLARK J., WOODS J.: J. Cryst. Growth, 3/4, 127 (1968).
- [19] BURR K.F., WOODS J.: J. Cryst. Growth, 9, 183, (1971).
- [20] LAUER R.B., WILLIAMS F.: J. Cryst. Growth, 8, 333, (1971).
- [21] NITSCHKE R.: J. Phys. Chem. Solids, 17, 163, (1960).
- [22] NITSCHKE R.: J. Cryst. Growth, 9, 238, (1971).

REVIEW OF THE GROWTH METHODS OF ZINC AND CADMIUM
SULFIDE, SELENIDE AND TELLURIDE SINGLE CRYSTALS

S u m m a r y

A review of the growth methods of (Zn,Cd)S, (Zn,Cd)Se, (Zn,Cd)Te single crystals is presented.

It is suggested that the method of sublimation - condensation being the most suitable to the conditions and facilities available, should be employed in the Department of Physics of Białystok Polytechnic.

STANDARD TITLE PAGE

1. Report No. NASA TM-88426	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle REVIEW OF METHODS FOR PREPARATION OF ZINC AND CADMIUM SULFIDE, SELENIDE AND TELLURIDE SINGLE CRYSTALS		5. Report Date May 1986	
		6. Performing Organization Code	
7. Author(s) Mieczyslaw Kucharczyk, Krystyna Zabloudowska		8. Performing Organization Report No.	
		10. Work Unit No.	
9. Performing Organization Name and Address SCITRAN Box 5456 Santa Barbara, CA 93108		11. Contract or Grant No. NASW- 4004	
		12. Type of Report and Period Covered Translation	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		14. Sponsoring Agency Code	
13. Supplementary Notes Translation of "Przegląd metod otrzymywania monokryształów siarczków selenków i tellurków cynku i kadmu", Zeszyty Naukowe Politechniki Białostockiej. (Ser) Matematyka Fizyka, Chemia, Poland, 1976, No. 1, pp. 3-21.			
16. Abstract A review of the growth methods of (Zn,Cd)S, (Zn,Cd)Se, (Zn,Cd)Te single crystals is presented. It is suggested that the method of sublimation - condensation being the most suitable to the conditions and facilities available, should be employed in the Department of Physics of Białystok Polytechnic.			
17. Key Words (Selected by Author(s))		18. Distribution Statement Unclassified and Unlimited	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 28	22. Price